GOVERNMENT OF INDIA : THE PATENT OFFICE, 214, ACHARYA JAGADISH BOSE ROAD, CALCUTTA-17. Complete specification No.142695 dated 19th January 1976. Application and Provisional specification No.115/Cal/75 dated 21st January 1975. Acceptance of the complete specification advertised on 13th August 1977.

Index at acceptance - 70C4 [LVIII(5)]

International classification - C 23 b 9/02

"Improvements in or relating to anodising aluminium and its alloys using alternating current in sulphuric acid electrolyte

Council of Scientific & Industrial Research, Rafi Marg, New Delhi-1, India, an Indian registered body incorporated under the Registration of Societies Act (Act XXI of 1860).

The following specification particularly describes the nature of this invention.

This is an invention by Baikunje Anantha Shenoi, Scientist Venkataraman Balasubramanian, Senior Scientific Assistant and Subbiah John, Junior Scientific Assistant, all of them are employed in Central Electrochemical Research Institute, Karaikudi-6, Tamil Nadu, India, and are Indian Nationals.

PRICE Rs. 2=00

This invention relates to improvements in or relating to anodising aluminium and its alloys using alternating current in sulphuric acid electrolyte.

Hitherto it has been proposed to use alternating current only for anodising of aluminium wires for small thicknesses of the order of 5 microns at low current densities. Alternating current anodising is only of theoretical interest and not commercially practised for architectural, hard and continuous anodising.

The drawbacks encountered in anodising aluminium and its alloys using alternating current are as follows:

During anodising aluminium and its alloys in sulphuric acid electrolyte using alternating current, electrolysis of water takes place followed by reduction of sulphuric acid and deposition of sulphur and sulphur compounds inside the pores of the oxide film. The aluminium oxide film formed by alternating current anodising is brown or yellow due to the presence of sulphur or sulphur compounds in the oxide film. Moreover, when constant current densities in excess of 2.0 A/dm^2 are used the voltage rise becomes excessive resulting in streaking and pitting and oxide film above 12 micron thickness could not built up. The anodised aluminium alloy in sulphuric acid electrolyte with alternating current when dyed in organic dyes and sealed the natural colour is changed and it is impossible to predict exactly what shade will be produced.

EXAMPLE 6.

52S aluminium alloy plate containing magnesium was polished, degreased and cleared as in Example 1 and anodised in 50% sulphuric acid containing 5% sodium tartrate using alternating current for 30 minutes at 1.6 A/dm^2 current density. Anodising was carried out at 20°C. There was no smell of hydrogen sulphide and when the anodised plates were dipped in lead acetate solution remained unaltered. The oxide film was about 10 micron and dye accsptance of the oxide layer was quite good.

EXAMPLE 7

Very often to get harder films at room temperature , sulphuric acid and oxalic acids are used. Even here when alternating current is used, there will be sulphur formation. But we have found by adding any one of our addition agents as mentioned in this specification, it is possible to avoid sulphur formation. The following example is given to illustrate the avoidance of sulphur formation:

Polished, degreased and cleaned 2S aluminium alooy plate was anodised in 7% sulphuric acid, 3% oxalic acid 5% sodium sulphate at a current density of 2.5 A/dm^2. The temperature was around 35° C. Voltage used was 15. Alternating current was used for anodising. After 30 minutes, the plate was removed and tested for sulphur content in the oxide film. Practically, there was neither the smell of hydrogen sulphide nor brown colour formation when dipped in lead acetate solution.

The following are among the main advantages of the invention:

1. This process of alternating current anodising in modified sulphuric acid electrolyte offers the opportunity of anodising in a tank of electrolyte with no cathode plates or other encumberances. Agitation is effected by pumping and recirculating, the electrolyte through a heat exchanger for cooling. Since the entire volume of the electrolyte can be effectively utilised for anodising more area of the work can be processed with maximum current loading.

2. This modified sulphuric acid bath when used for anodising aluminium and its alloys using alternating current, there will be no burning due to high current densities. Further, the work can be processed quickly or more work can be processed by ensuring complete current utilisation and optimum loading.

3. The cost of electrical equipment for alternating current anodising is much cheaper than direct current since what is required is only a step-down transformer and voltage regulator.

4. Alloys which are normally regarded as difficult-to-anodise (i.e. high copper and silicon wrought alloys and castings) can be easily processed, because of the tendency of alternating current to reduce the change of burning at high current density and voltages.

5. Owning to the natural cleaning action of alternating current when large volumes of hydrogen and oxygen are alternatively evolved, the chemical pretreatement of the aluminium alloys containing copper and silicon can be minimised to avoid the revelation of metallurgical defects.

Dated this 14th day of January, 1975.

Sd/-
ASSISTANTS PATENTS OFFICER.
Council of Scientific & Industrial Research.

142695

THE PATENTS ACT, 1970

COMPLETE SPECIFICATION

SECTION 10.

"Improvements in or relating to anodising aluminium and its alloys using alternating current in sulphuric acid electrolyte"

Council of Scientific & Industrial Research, Rafi Marg, New Delhi-1, India, an Indian registered body Incorporated under the Registration of Societies Act (Act XXI of 1860).

The following specification particularly describes and ascertains the nature of this invention and the manner in which it is to be performed :-

This is an invention by Balkunje Anantha Shenoi, Scientist, Venkataraman Balasubramanian, Senior Scientific Assistant and Subbiah John, Senior Technical Assistant, all of the Central Electrochemical Research Institute, Karaikudi-6, Tamil Nadu, India and all are Indian Nationals.

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This invention relates to improvements in or relating to anodising aluminium and its alloys using alternating current in sulphuric acid electrolyte.

Higherto it has been proposed to use alternating current only for anodising of aluminium wire to a thickness of the order 5 microns at low current densities. Anodising with alternating current is only of theoritical interest and not commercially practised for decorative, arthitectural, hard and continuous anodising.

The drawbacks encountered in anodising aluminium and its alloys using alternating current are as follows:

During anodising aluminium and its alloys in sulphuric acid electrolyte using alternating current, electrolysis of water takes place followed by reduction of sulphuric acid and deposition of sulphur and its compounds inside the pore of the oxide film.

The presence of sulphur and its compounds inside the pores of the oxide film imparts brown or yellow colour to the oxide film causing unpredictable colour change when dyed in organic dyes and sealed.When alternating current is used for

anodising, current densities in excess of 2.0A/dm^2 results in streaking and pitting and oxide film above 12 micron thickness can not be built up.

The main object of the invention is to obviate these disadvantages encountered in anodising aluminium and its alloys containing silicon, copper or Magnesium with alternating current using the modified sulphuric acid electrolyte of the present invention.

The main finding underlying the invention broadly consists in anodising aluminium and its alloys in 5 to 50% W/V electrolyte comprising any one of the additives such as alkali metal sulphates, oxalates, nitrates, citrates, tartrates and borates in the range of 0.5 to 10%. The voltages of the order of 10 to 30 volts and current density of 1.5A/dm^2 to 6.4A/dm^2 range were used. The temperature of anodising is kept be ween 1t°C to 30° C.

The new results flowing from the new finding are as follows:

The additive compounds mentioned in this specification when added to sulphuric acid electrolyte, the basic mechanism of electrolysis is shifted back in favour of the electrolysis of water rather than the reduction of sulphuric acid. Hence there is no deposition of sulphur and its compounds inside the pores of the oxide film. This is tested by the following methods: (1) There is no smell of sulphurated hydrogen over the A.C. anodised aluminium plates immediately after anodising indicates the absence of reduction of sulphuric acid (2) The anodised plates were dipped in lead acetate solution to observe colour change. The absence of yellow or brown colour on the oxide film clearly indicate the absence of sulphur and its compounds inside the pores of the oxide film.

It was also found that the anodising can be carried out at high current densities of the order of 4.8A/dm^2 without pitting or streaking in the modified sulphuric acid bath employing alternating current and thickeness of the order of 30 microns are obtained in 30 minutes. The additive compounds mentioned in this specification when added to sulphuric acid anodising bath, the anodising alternating current voltage is brought down substantially thereby saving power consumption and this is shown in Fig. 1 of the accompanying drawings.

The present invention consists in anodising aluminium and its alloys with Magnesium, copper and silicon in a 'box' of electrolyte with no cathode plates or other encumbrances. Since high current denisites can be employed in the pesent anodising bath without the chances of burning and streaking either the work can be processed faster or more work can be processed.

The present invention concists of a process for anodising aluminium and its alloys using alternating current in sulphuric acid electrolyte which comprises polishing (electro polishing, chemical polishing or mecahnical polishing), degreasing, cleaning and anodising aluminium and its alloys in the modified sulphuric acid electrolyte using alternating current. The anodised aluminium is dyed with organic or inorganic dye solution and finally hot water or steam sealed. The process sequence is given in Fig. 2 of the accompanying drawing.

The following typical examples are given to illustrate the invention and not to limit the scope of the invention.

EXAMPLE 1

Chemically polished and degreased 28 aluminium alloy plate 5 cm x 2.5 cm (99% aluminium) was cleaned in 10% sodium hydroxide and washed in water. This was followed by acid cleaning in 10% nitric acid for desmutting. The specimens were washed in tap water and rinsed in distilled or deionised

water. Anodising was carried out with these specimens in 10% sulphuric acid electrolyte containing 4% sodium nitrate with alternating current at 6.4 A/dm^2 current density. The anodising bath temperature was maintained at $20^{\circ}C \pm 2^{\circ}C$. The specimens were anodised for half an hour and later, it was washed in tap water followed by distilled water. One specimen was dyed in 2% anodol golden yellow dye and the other was dipped in dilute lead acetate solution. The specimen dipped in lead acetate solution did not change colour showing the absence of sulphur. The other specimen dipped in the dye solution was dyed well and dye absorpition was found to be good by visual observation. There were no streaking or pitting on the anodised plates due to high current density. The oxide layer thickness was found to be 25 microns by stripping method.

EXAMPLE 2

3S aluminium alloy plate was mechanically polished, degreased and cleaned as in Example 1 and anodised in an electrolyte comprising 15% sulphuric acid and 3% potassium sulphate at a current density of 2.8 A/dm^2 employing alternating current at $22^{\circ}C$ for one hour. The anodised plates were not coloured yellow and when dipped in lead acetate no brown colour was obtained indicating the absence of sulphur compounds. The anodising bath voltage was 20. The dye intake on the oxide film was good. The thickness of the oxide layer was found to be 30 microns by stripping method.

EXAMPLE 3

51 SWP aluminium alloy extruded wire containing 5/8% Mg and 1% Si was anodised in 20% sulphuric acid electrolyte containing 6% sodium oxalate after cleaning the alloy as mentioned in Ex. 1. A current density of 3.3 A/dm^2 was

employed using alternating current and the specimens were anodised for 30 minutes at 20°C. The oxide film thickness was found to be 15 microns by stripping method. It gave negative result with lead acetate solution showing the absence of sulphur. The dye intake of the oxide film was good.

EXAMPLE - 4

26S (4.25% copper rest aluminium (aluminium alloy plate was mechanically polished, degreased and cleaned in 10% sodium hydroxide and anodised in 15% sulphuric acid electrolyte containing 5% sodium citrate using alternating current at 4 A/dm^2. Anodising for half an hour was carried out at 20° C. The oxide layer thickness was found to be 18 microns. The anodised sample was tested for sulphur in lead acetate solution and found to be absent. The sample was dyed to see the dye absorbing property and found to be all right.

EXAMPLE 5

2S aluminium alloy plate was electropolished, degreased and cleaned and anodised in 15% sulphuric acid electrolyte with 4% sodium tetraborate using alternating current at 2.5 A/dm^2 and at 20° C. After 30 minutes, the plates were removed and tested for sulphur by dipping in the lead acetate solution. The thickness of the oxide film was found to be 11 microns. There was no yelllow or brown colour showing the absence of sulphur. There were no streaking or pitting on the plates and were uniformly anodised.

EXAMPLE-6

52S aluminium alloy plate containing magnesium was polished, degreased and cleaned as in Ex.1 and anodised in 50% sulphuric acid containing 5% sodium tartrate using alternating current for 30 minutes at 1.6 A/dm^2 current density.

Anodising was carried out at 25° C. There was no smell of hydrogen sulphide and when the anodised plates were dipped in lead acetate solution remained unaltered. The oxide film was about 7 micron and dye acceptance of the oxide layer was quite good.

EXAMPLE 7

Very often to get harder films at room temperature, sulphuric acid and oxalic acids are used as electrolyte in conventional anodising. When alternating current is used for harder films in the above electrolyte, sulphur and its compounds will get deposited inside the pores of the oxide film. But we have found by adding any one of our addition agents as mentioned in this specification, it is possible to avoid the formation of sulphur and its compounds in the pores of the oxide film. The following example is given to illustrate the aboidance of the formation of sulphur and its compounds.

Mechanically polished, degreased and cleaned 2S aluminium alloy plates was anodised in 7% sulphuric acid, 3% oxalic acid 5% sodium sulphate at a current density of 25 A/dm^2 using alternating current. The temperature was around 30° C. Voltage was 15. After 30 minutes, the plate was removed and tested for sulphur content in the oxide film. Practically, there was neither the smell of hydrogen sulphide nor brown colour formation when dipped in lead acetate solution.

The following are among the main advantages of the invention:

1. This process of alternating current anodising in modified sulphuric acid electrolyte offers the opportunity of anodising in a tank of electrolyte with no cathode plates or other accessories. Agitation is effected by pumping and recirculating, the electrolyte through a heat exchanger for cooling. Since the entire volume of the electrolyte can be effectively utilised for anodising more area of the work can be processed with maximum current loading.

2. This modified sulphuric acid bath when used for anodising aluminium and its alloys using alternating current, there will be no burning due to high current densities, and hence the work can be processed qickly or more work can be processed.

3. The cost of electricalequipment for alternating current anodising is much cheaper than direct current since what is required is only a step-down transformer and voltage regulator.

4. Alloys which are normally regarded as difficult-to-anodise (i.e. high copper and silicon wrought alloys and castings) can be easily processed, because of the tendency of alternating current to reduce the chance of burning at high current density and voltages.

5. Due to the natural cleaning action of alternating current when large volumes of hydrogen and oxygen are alternatively evolved on the aluminium surface, the chemical cleaning of the aluminium alloys containing copper and silicon can be minimised to avoid the preferential etching of the surface.

WE CLAIM

1. A process for anodising aluminium and its alloys containing copper, magnesium or silicon using alternating current in sulphuric acid electrolyte which consists in polishing, degreasing, cleaning and anodising the aluminum and its allloys in 5-50% w/w sulphuric acid electrolyte containing additive agents such as alkali metal sulphates, oxalates, nitrates, citrates, tartrates and borates in the range of 0.5 to 10%, dyed with organic or inorganic pigments and finally hot water or steam sealed.

2. A process as claimed in claim 1 wherein the operating temperature of the anodising bath ranges from 15° C to 30° C.

3. A process as claimed in claim 1 and 2 wherein the current density is in the range of 1.5A/dm^2 to 6.4A/dm^2 while the operating voltage ranges from 10V to 30V.

Dated this 16th day of January, 1976.

Sd/-
ASST. PATENTS OFFICER
COUNCIL OF SCIENTIFIC AND
INDUSTRIAL RESEARCH, NEW DELHI

COMPLETE SPECIFICATION.

COUNCIL OF SCIENTIFIC & INDUSTRIAL RESEARCH.

No. OF SHEETS:- 2.

No. 142695

SHEET No. :- 1.

CURVES :-

A - 10% V/v H_2SO_4.

B - 10% V/v H_2SO_4 + 3% Addition Agent.

CONDITIONS :-

Temp.:- 20 ± 2°C.

Current Density :- 48 asf.

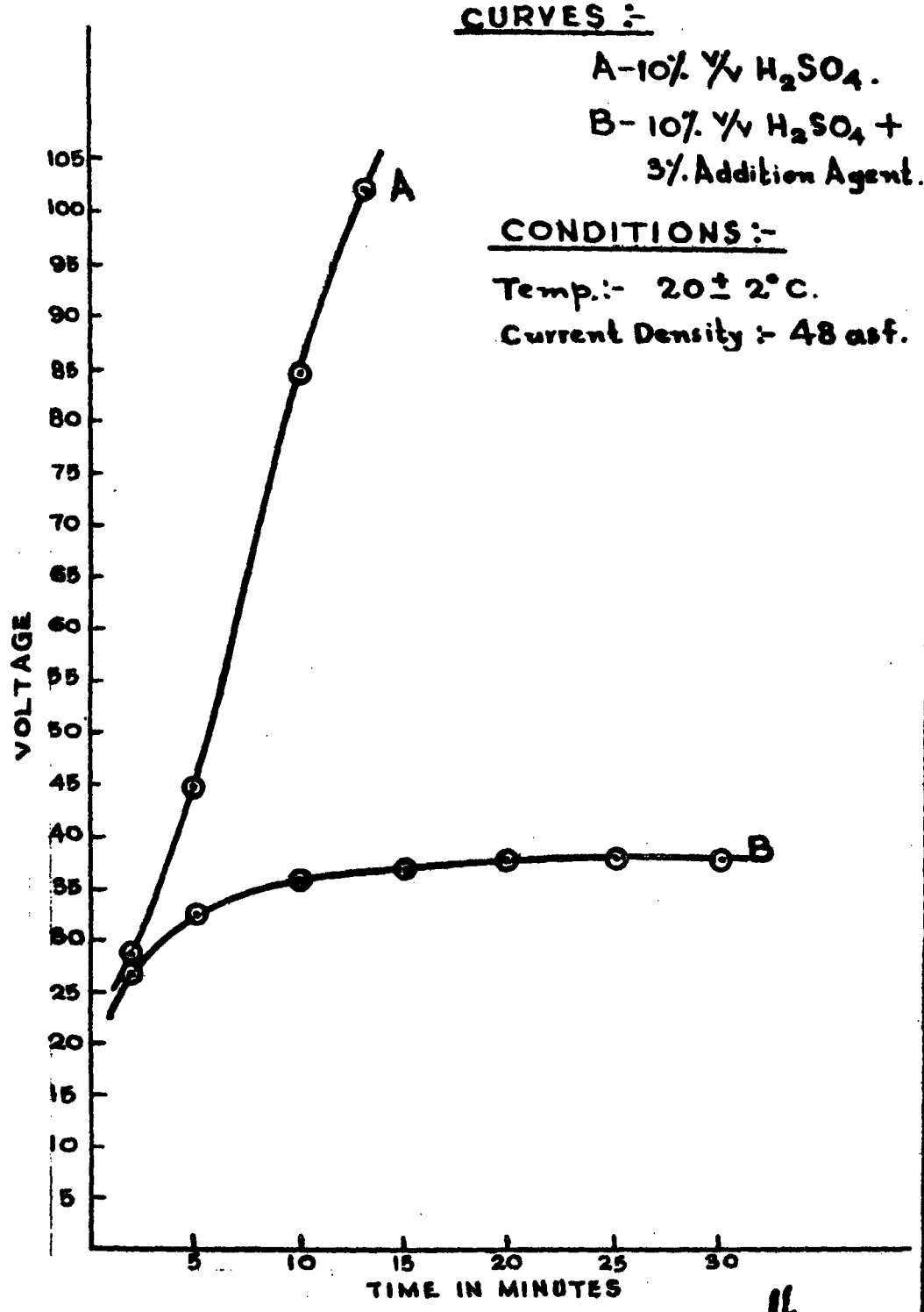

FIG. 1.

[RYD.PAI]

Asst. PATENTS OFFICER,

C.S.I.R.

COMPLETE SPECIFICATION.

COUNCIL OF SCIENTIFIC & INDUSTRIAL RESEARCH.

No. OF SHEETS:-2.

No. 142695

SHEET No.: 2.

FLOW SHEET.

IMPROVEMENTS IN OR RELATING TO ANODISING ALUMINIUM AND ITS ALLOYS USING ALTERNATING CURRENT IN SULPHURIC ACID ELECTROLYTE.

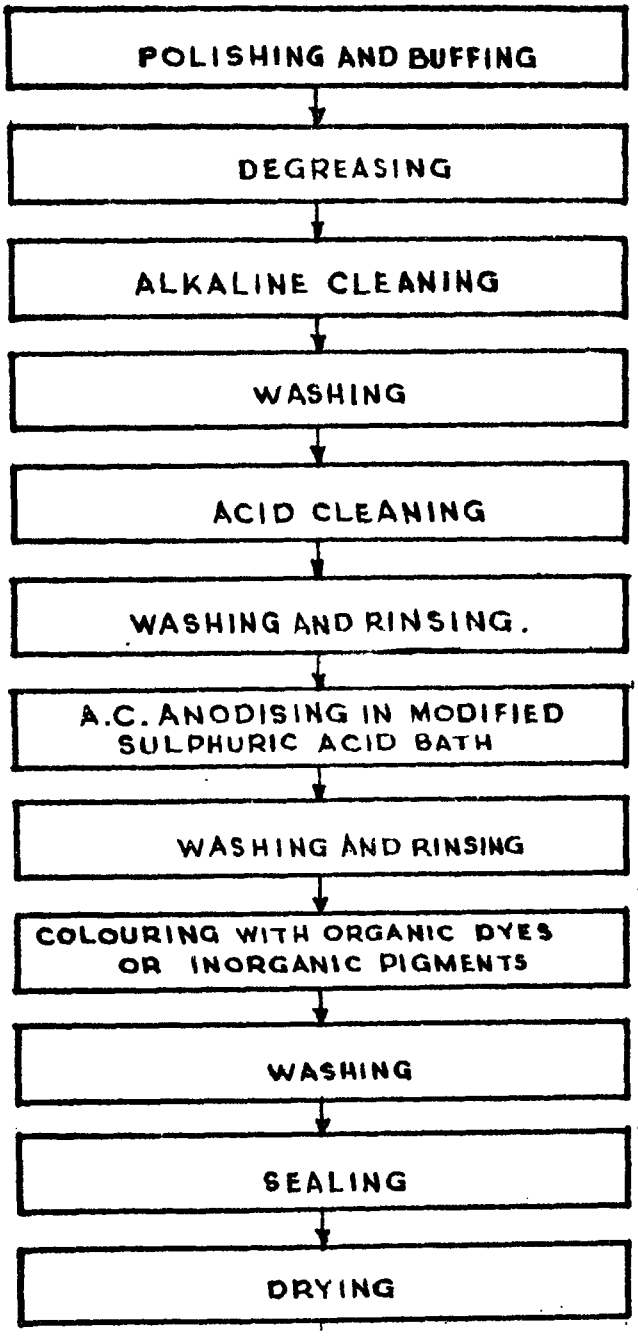

FIG. 2.

R.S. RAI,
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